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(54) **PROCESS FOR MAKING CLEAR POLYURETHANE/UREA ELASTOMERS**

**VERFAHREN ZUR HERSTELLUNG VON TRANSPARENTEN
POLYURETHAN/HARNSTOFFELASTOMEREN**

PROCEDE DE PREPARATION D'ELASTOMERES CLAIRS DE POLYURETHANNE/UREE

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EP 1 066 332 B1

Description

FIELD OF THE INVENTION

- 5 [0001] The invention relates to polyurethane elastomers. In particular, the invention relates to a process for making clear polyurethane/urea elastomers that have good dynamic properties, particularly high resilience. These elastomers are especially valuable in the manufacture of wheels for in-line skates.

BACKGROUND OF THE INVENTION

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[0002] In-line skate wheels require elastomers having excellent resilience (rebound), which prevents the wheels from overheating or even melting during use. In addition, highly resilient wheels roll more easily, so they require less effort from the skater.

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[0003] High-performance polyurethane cast elastomers (typically made from MDI, polytetramethylene ether glycol (PTMEG), and 1,4-butanediol) are currently the material of choice for in-line skate wheels. The best (and usually the most-expensive) elastomers use PTMEG and have resiliences of 70-80%. Less expensive elastomers can be made with polyester polyols or polyoxypropylene diols (PPGs) instead of PTMEG, but these have significantly lower resilience. For example, a typical elastomer based on conventional PPGs has a resilience of only 50-55%. The industry would benefit from inexpensive elastomers having high resilience.

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[0004] Opaque skate wheels are spinning out of favor with skaters and skateboarders. Like baggy jeans and heavy metal, clear wheels are "in." Skaters just like the looks of transparent wheels. Unfortunately, to make clear wheels, formulators usually have to make composition changes that sacrifice resilience and other key elastomer properties. Preferably, clear elastomers could be made without hurting performance.

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[0005] Polyurethane elastomers, in the purest sense, use diol chain extenders and have urethane (-O-CO-NH-) groups but do not have urea (-NH-CO-NH-) groups. In contrast, polyurethane/urea elastomers, because they are made with diamine chain extenders (usually an aromatic diamine), have both urethane and urea groups. So far, polyurethane/urea elastomers have not significantly penetrated the in-line skate market. This is probably because the high viscosities of prepolymers based on PTMEG or polyester polyols make the elastomers hard to process and prevent formulators from easily reaching the targeted hardness.

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[0006] Recently issued U.S. Pat. No. 5,646,230 summarizes various approaches now used in the field to make polyurethane/urea elastomers and identifies some important concerns. For example, it cites U.S. Pat. No. 3,115,481 to illustrate that isocyanate-terminated prepolymers made from aromatic diisocyanates are usually too reactive with aromatic diamine chain extenders to allow processing of cast elastomers. U.S. Pat. No. 3,997,514 resolves the reactivity problem by making hydroxy-terminated prepolymers from an excess of glycol (e.g., PTMEG) and aromatic diisocyanate. The hydroxy-terminated prepolymer is then reacted with an aliphatic diisocyanate to make an aliphatic diisocyanate-terminated prepolymer that has more controlled, reduced reactivity with aromatic diamines.

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[0007] In contrast, the '230 patent teaches to make aliphatic diisocyanate-terminated prepolymers by reacting, preferably in a single step, a polyether polyol (PPGs or PTMEG), an aromatic diisocyanate, and an aliphatic diisocyanate. These prepolymers are then chain extended with aromatic diamines. While both the aromatic and aliphatic diisocyanates react into the prepolymer, the aromatic diisocyanate reacts faster so the terminal NCO groups derive primarily from the aliphatic diisocyanate. A relatively large proportion (compared with the amount of aromatic diisocyanate) of the more-expensive aliphatic diisocyanate is used. Missing from the '230 patent is any discussion of how to make clear elastomers while maintaining the high resilience needed for high-quality, in-line skate wheels.

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[0008] In sum, the high-performance elastomer market would benefit from improved elastomers. Of particular value is a way to make the clear elastomers now in vogue without sacrificing important mechanical properties. Preferably, the elastomers could be made from readily available materials that are listed under the Toxic Substances Control Act (TSCA). Preferably, the process used to make them would avoid the reactivity problems of aromatic diisocyanate-terminated prepolymers and the viscosity issues of prepolymers made from PTMEG and polyester polyols. An ideal process would give clear, low-cost elastomers with an excellent overall balance of properties, particularly high resilience.

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SUMMARY OF THE INVENTION

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[0009] The invention provides a path to clear elastomers that meet the demanding dynamic property requirements of in-line skates. In particular, the invention is a process for making clear polyurethane/urea elastomers. The process comprises three steps. First, a polyol reacts with an aromatic diisocyanate comprising less than 90 wt% of 4,4'-MDI to give an isocyanate-terminated prepolymer. The polyol has a polydispersity (Mw/Mn) less than 1.5. The NCO/OH mole ratio used is within the range of 1.3 to 3.0. Next, the resulting prepolymer is mixed with an aliphatic diisocyanate to

form a prepolymer/aliphatic diisocyanate mixture that has an NCO content within the range of 2 to 13 wt.%. In the third step, this prepolymer/aliphatic diisocyanate mixture reacts with an aromatic diamine wherein the aromatic diamine is used at an NCO/NH ratio in the range of 0.9 to 1.2.

[0010] We surprisingly found that getting clear elastomers does not have to mean compromising physical properties. By reacting a mixture of a particular prepolymer/aliphatic diisocyanate mixture with a common aromatic diamine chain extender, we made clear elastomers with excellent overall physical and mechanical properties, particularly resilience greater than 55% at 80A Shore hardness. Surprisingly, the process of the invention gives clear, resilient elastomers even at Shore hardnesses well in excess of 80A, which is hard to do with current know-how. Moreover, the process of the invention avoids the high-viscosity prepolymers that have, until now, limited formulators of polyurethane/urea elastomers.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The invention is a three-step process for making clear polyurethane/urea elastomers. In the first step, an aromatic diisocyanate reacts with a polyether polyol to give an isocyanate-terminated prepolymer.

[0012] Aromatic diisocyanates suitable for use in the invention are those well known in the polyurethane elastomer art. Examples include 2,4- and 2,6-toluene diisocyanates and mixtures of these isomers (TDIs), diphenylmethane diisocyanates (MDIs), TDIs and MDIs modified with carbodiimide, urethane, allophanate, isocyanurate, urea, or biuret groups, phenylene diisocyanates, naphthalene diisocyanates, and the like, and mixtures thereof. Other suitable examples are found in U.S. Pat. Nos. 5,646,230 and 3,997,514, the teachings of which are incorporated herein by reference. Preferred aromatic diisocyanates are commercially available TDIs and MDIs, such as TDI-80 (which contains 80% of 2,4-toluene diisocyanate and 20% of 2,6-toluene diisocyanate), pure 2,4-TDI, and MONDUR ML (50% 4,4'-MDI plus 50% of MDI isomers other than 4,4'-MDI, product of Bayer Corporation). When MDIs are used, it is preferred to use an MDI that has at least 15 wt.% of MDI isomers other than 4,4'-MDI. As Table 3 shows, potlife can become too short if the level of 4,4'-MDI in the elastomer system exceeds 90 wt.%.

[0013] Suitable polyols are well known in the art, and include polyether polyols, polyester polyols, polycarbonate polyols, and the like. Polyether polyols are preferred. Suitable polyether polyols are commonly made by polymerizing one or more cyclic ethers, such as epoxides (e.g., ethylene oxide, propylene oxide), oxetanes, oxolanes (e.g., tetrahydrofuran), or the like, in the presence of water or an alcohol starter. The polyols are made using any suitable catalyst, including, for example, potassium hydroxide (KOH), boron trifluoride, or a double metal cyanide (DMC) catalyst. DMC catalysts are preferred because they easily give polyether polyols with exceptionally low unsaturation or monol content. The polyols can be homopolymers (e.g., polyoxypropylene diols), random copolymers of two or more cyclic ethers (e.g., a random copolymer of propylene oxide and ethylene oxide), block copolymers (e.g., a polyoxypropylene core with a polyoxyethylene cap), "tipped" copolymers (e.g., Polyol F described below), or the like.

[0014] Polyols useful in the invention have narrow molecular weight distributions. In particular, the polyols have polydispersities (M_w/M_n) less than 1.5. (M_n is the number average molecular weight, and M_w is the weight average molecular weight; both are conveniently determined by well-known gel permeation chromatography methods.) Preferred polyols have M_w/M_n values less than 1.4; more preferred are polyols having M_w/M_n values less than 1.2. Such narrow molecular weight distributions are needed to give prepolymers with viscosities low enough to process effectively in the chain extension reaction to make elastomers. In contrast, commercial polytetramethylene ether glycols and polyester polyols generally have M_w/M_n values within the range of 1.7 to 2.5.

[0015] Preferred polyols have equivalent weights within the range of 750 to 10,000. A more preferred range is from 1000 to 5000; most preferred is the range from 1000 to 4000. Minor proportions of lower molecular weight diols or triols, preferably less than 40 weight percent, can be included with the polyol if desired to modify elastomer processing or physical properties.

[0016] The polyols preferably have a nominal hydroxyl functionality within the range of 2 to 6; a more preferred range is from 2 to 3.

[0017] Particularly preferred are polyether diols that have an actual hydroxyl functionality close to 2. The actual hydroxyl functionality of polyether diols usually varies and often depends on the nature the catalyst used to make the diol. While a polyether diol made by conventional KOH catalysis typically has an actual hydroxyl functionality of only about 1.6 or 1.7, one made via DMC catalysis may have an actual hydroxyl functionality very close to 2.

[0018] Preferred polyols for use in the process of the invention also have low unsaturation. In particular, preferred polyols have unsaturations less than 0.02 meq/g, more preferably less than 0.01 meq/g, and most preferably less than 0.007 meq/g. These polyols can be made by various known methods, including DMC catalysis as described in U.S. Pat. Nos. 5,158,922, 5,470,813, and 5,482,908, the teachings of which are incorporated herein by reference. Elastomers made according to the process of the invention with polyols of low unsaturation generally have better tear strength, higher resilience, and far better tensile strength compared with elastomers based on polyols having unsaturation levels greater than 0.02 meq/g (see Table 4 below).

[0019] The prepolymer is made by reacting the aromatic diisocyanate and the polyol at an NCO/OH ratio within the range of 1.3 to 3.0. A more preferred range is from 1.5 to 2.0; most preferred is the range from 1.5 to 1.8. This NCO/OH ratio is relatively high. Compare, for example, U.S. Pat. No. 5,646,230, which teaches to make prepolymers (from polyols, aromatic diisocyanates, and aliphatic diisocyanates) in one step using an aromatic diisocyanate to polyol ratio of about 1.0. By using such a high proportion of aromatic diisocyanate, we found that we could better control the viscosity of the resulting prepolymer, which will have a much lower molecular weight than a similar prepolymer made with an NCO/OH ratio that approaches 1. The high proportion of aromatic diisocyanate is also a cost advantage because less of the more-expensive aliphatic diisocyanate can be used.

[0020] Generally, the more preferred ranges for the NCO/OH ratio will depend on the nature of the polyol and aromatic diisocyanate. For example, when TDI-80 is used, the NCO/OH ratio used is preferably less than 1.7 because higher ratios may not always give a clear product. On the other hand (as Table 10, Example 31 shows), clear elastomers can be made even at an NCO/OH ratio of 3.0 if with the right choice of aromatic diisocyanate and polyol. Generally, prepolymers made at NCO/OH ratios of less than 1.3 are not suitable for use in the invention because their molecular weights and viscosities are too high for successful elastomer processing. At NCO/OH ratios greater than 3.0, prepolymer viscosities are low enough, but the resulting elastomers are usually hazy.

[0021] While the prepolymer can be made at any desired temperature, it is generally preferred to react the polyol and the aromatic diisocyanate at a temperature within the range of 40°C to 120°C; a more preferred range is from 60°C to 100°C; most preferred is the range from 70°C to 90°C.

[0022] It is often desirable to use a catalyst in making the prepolymer, although no catalyst is required. When a catalyst is used, it is preferably an organometallic catalyst, such as, for example, an organometallic tin, lead, iron, bismuth, or mercury compound. Organotin compounds such as dibutyltin dilaurate are preferred. Delayed-action catalysts can also be used. Other suitable catalysts are described in U.S. Pat. No. 5,646,230, the teachings of which are incorporated herein by reference. When a catalyst is used, it is typically used in an amount within the range of 25 to 1000 ppm.

[0023] The isocyanate-terminated prepolymer made in the first step is mixed, by any suitable method (e.g., mechanical stirring), with an aliphatic diisocyanate to form a prepolymer/aliphatic diisocyanate mixture. The value of making this simple mixture cannot be underestimated; the mixture has significantly lower reactivity with the aromatic diamine chain extender compared with the prepolymer alone, and this is a key to getting adequate potlife and good processability in making the elastomers.

[0024] The prepolymer/aliphatic diisocyanate mixture has a wt.% NCO content within the range of 2 to 13 wt.%, more preferably within the range of 3 to 10 wt.%. Brittle products can result when the mixture used has a wt.% NCO content greater than 13 wt.% (see Comparative Example 8). At wt.% NCO contents less than 2, the mixture viscosity can be too high for good processability.

[0025] The aliphatic diisocyanate and prepolymer are usually mixed at about the same the temperature used to make the prepolymer. Thus, they are combined at a temperature within the range of 40°C to 120°C; a more preferred range is from 60°C to 100°C; most preferred is the range from 70°C to 90°C. It is usually preferred to heat this mixture under vacuum to remove any entrapped gases.

[0026] The prepolymer/aliphatic diisocyanate mixtures prepared according to the process of the invention have low viscosities. Preferably, the mixtures have Brookfield viscosities less than 5000 cps at 80°C, more preferably less than 3000 cps at 80°C, most preferably less than 1000 cps at 80°C. At such low viscosities, the prepolymer/aliphatic diisocyanate mixtures blend easily with the aromatic diamine chain extenders.

[0027] Aliphatic diisocyanates suitable for use in the invention are also well known. Examples include hydrogenated MDIs (e.g., H₁₂MDI), isophorone diisocyanate (IPDI), tetramethylxylene diisocyanates (e.g., m-TMXDI), and the like, and mixtures thereof. Other suitable aliphatic diisocyanates are described in U.S. Pat. Nos. 5,646,230 and 3,997,514, the teachings of which are incorporated herein by reference. IPDI, m-TMXDI, and H₁₂MDI are preferred.

[0028] In the third step, the prepolymer/aliphatic diisocyanate mixture reacts with an aromatic diamine chain extender in an amount and manner effective to produce a clear polyurethane/urea elastomer. Usually, the aromatic diamine is added in liquid form to the well-stirred and degassed mixture of prepolymer and aliphatic diisocyanate. The processing temperature is preferably within the range of 40°C to 100°C, more preferably from 50°C to 90°C. The reaction mixture is then usually poured into a pre-heated mold and is heated until the elastomer cures. The elastomer is removed from the mold, preferably within 3 to 10 minutes of pouring, and is post-cured, if desired, by heating it in an oven for several hours (typically overnight). Preferably, the potlife of the elastomer (i.e., the maximum time the formulator has to fill the mold with the reaction mixture after adding the aromatic diamine to the prepolymer/aliphatic diisocyanate mixture) is at least 20 seconds, more preferably at least 30 seconds. If the potlife is less than 20 seconds, there is usually inadequate time to mix the components and fill the mold before the part cures, particularly for intricate parts such as in-line skate wheels.

[0029] Aromatic diamines suitable for use are well known in the polyurethane elastomer art. Sterically hindered aromatic diamines are preferred. Suitable aromatic diamines include, for example, diethyltoluene diamines, dimethyl-

thiotoluene diamines, and the like, and mixtures thereof. Other suitable examples are described in U.S. Pat. Nos. 5,646,230, 4,146,688, and 4,631,298, the teachings of which are incorporated herein by reference. Particularly preferred are DETDA, which is an isomer mixture containing mostly 3,5-diethyl-2,4-toluenediamine and 3,5-diethyl-2,6-toluenediamine, and DMTTDA, which is an isomer mixture containing mostly 3,5-dimethylthio-2,4-toluenediamine and 3,5-dimethylthio-2,6-toluenediamine. Both are commercially available from Albemarle Corporation as ETHACURE 100 and ETHACURE 300, respectively. DETDA has the right degree of reactivity with the prepolymer/aliphatic diisocyanate mixture for fast elastomer processing (and machine casting), while DMTTDA reacts more slowly and is usually better for hand casting.

[0030] It is also preferred to use an aromatic diamine that has relatively low color. A low-color diamine will tend to give low-color elastomers. Water-white wheels (i.e., clear and colorless wheels)-again for purely aesthetic reasons-are in demand. Preferably, the aromatic diamine will have a color less than #7, more preferably less than #3, on the Gardner scale. Low-color aromatic diamines are available commercially; alternatively, aromatic diamines with higher color can be decolorized by conventional means (distillation, carbon treatment, addition of reducing agents, or the like).

[0031] The amount of aromatic diamine used is preferably adjusted to give an NCO/NH ratio within the range of 0.9 to 1.2, preferably from 1.0 to 1.1, and most preferably from 1.03 to 1.10. Generally, the amount of aromatic diamine used will depend on the % NCO content of the prepolymer/aliphatic diisocyanate mixture. Usually, however, the aromatic diamine is used in an amount within the range of 5 to 30 wt.%. A more preferred range is from 7 to 20 wt.%.

[0032] Optionally, the elastomers contain one or more compounding ingredients commonly used in the art. For example, antioxidants, plasticizers, UV stabilizers, adhesion promoters, mold-release agents, fillers, dyes, and the like can be used. Generally, the compounding ingredients, when used, comprise less than 75 wt.% of the elastomer.

[0033] Elastomers made by the process of the invention are clear. By "clear," we mean that a person can easily read newsprint through the 4" length of a 4"x1"x1" sample, and the sample appears clear even through the 4" thickness. While it is easy to make opaque elastomeric products, making clear elastomers with the dynamic property requirements of high-performance polyurethane elastomers is much more challenging. We surprisingly found that the process of the invention offers clarity without sacrificing important elastomer properties such as resilience.

[0034] Until now, making clear elastomers with excellent resilience has often meant settling for Shore hardnesses of 80A or below using higher-cost systems. With the process of the invention, however, Shore hardnesses of greater than 75A are typical, and Shore hardnesses up to 40-45D (= 90A) can be easily made; even 60D is within reach (see Example 23). On the other hand, elastomers with Shore hardnesses in the range of 60A to 70A can also be made (see Example 28), and even lower hardnesses are possible if a plasticizer is included.

[0035] Elastomers made by the process of the invention are also highly resilient. Rebound % values greater than 55% are typical. Preferably, the elastomers have rebound % values greater than 60%; more preferably, the rebound % values are greater than 65%. Prior-art processes, such as the one-step method described in U.S. Pat. No. 5,646,230, give elastomers with, at best, rebound % values of only about 50% (see Tables 2b and 4b of the reference).

[0036] Another important advantage of the process of the invention is that it can be used with exclusively TSCA-listed materials. The Toxic Substances Control Act of 1976 (TSCA) gives the EPA power to control the manufacturing, importing, distribution, and processing of new chemical substances. TSCA-listed materials are those that the EPA considers safe to make and use. The prepolymer, aliphatic diisocyanate, and aromatic diamine components used in the process of the invention can all be selected from TSCA-listed materials.

[0037] Finally, the invention offers a high-performance elastomer at low cost. Because a variety of polyols are suitable, formulators are not locked into using relatively expensive PTMEGs or polyester polyols. As explained above, the ability to use a high proportion of aromatic diisocyanate reduces the amount of aliphatic diisocyanate needed and reduces the total cost of the isocyanate component. Moreover, because the invention uses readily available materials and equipment, high-performance elastomers do not have to cost a fortune.

[0038] The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

KEY TO THE MATERIALS

[0039]

50% 4,4'-MDI: Commercially available from Bayer Corporation as MONDUR ML, this product is a mixture of isomers of diphenylmethane diisocyanate that contains about 50 wt.% of the 4,4'- isomer and about 50 wt.% of other isomers.

100% 4,4'-MDI: Diphenylmethane diisocyanate containing essentially all 4,4'- isomer.

TDI-80: A mixture of 2,4-toluene diisocyanate (80 wt.%) and 2,6-toluene diisocyanate (20 wt.%).

TD 1-100: pure 2,4-toluene diisocyanate (about 100%).

IPDI: isophorone diisocyanate.

H₁₂MDI: an isomer mixture of dicyclohexylmethane-4,4'-diisocyanate.

m-TMXDI: m-tetramethylxylene diisocyanate.

Polyol A: A 2000 mol. wt. (hydroxyl number = 56 mg KOH/g) propylene glycol-started, propylene oxide-based polyether diol; unsaturation: 0.03 meq/g.

Polyol B: A 2000 mol. wt. (hydroxyl number = 56) propylene glycol-started, propylene oxide-based polyether diol; unsaturation: 0.005 meq/g.

Polyol C: A 4000 mol. wt. (hydroxyl number = 28) propylene glycol-started, propylene oxide-based polyether diol; unsaturation: 0.005 meq/g.

Polyol D: A 3000 mol. wt. (hydroxyl number = 37) propylene glycol-started, propylene oxide-based polyether diol containing about 10 wt.% of random, internal oxyethylene moieties; unsaturation: 0.003 meq/g.

Polyol E: A 3000 mol. wt. (hydroxyl number = 37) propylene glycol-started, propylene oxide-based polyether diol containing about 20 wt.% of random, internal oxyethylene moieties; unsaturation: 0.003 meq/g.

Polyol F: A 3200 mol. wt. (hydroxyl number = 35) propylene glycol-started, propylene oxide-based polyether diol having a total oxyethylene content of about 20 wt.%. The diol contains about 5 wt.% of random internal oxyethylene moieties and has a 45/55 EO/PO tip containing about 15 wt.% of oxyethylene units, for a total oxyethylene content of about 20 wt.%; unsaturation: 0.004 meq/g.

Polyol G: A 4000 mol. wt. (hydroxyl number = 28) propylene glycol-started, propylene oxide-based polyether diol having a total oxyethylene content of about 20 wt.%. The diol contains about 5 wt.% of random internal oxyethylene moieties and has a 45/55 EO/PO tip containing about 15 wt.% of oxyethylene units, for a total oxyethylene content of about 20 wt.%; unsaturation: 0.004 meq/g.

Polyol H: A 2250 mol. wt. (hydroxyl number = 50) propylene glycol-started, ethylene oxide-capped, propylene oxide-based polyether diol having a total oxyethylene content of about 25 wt.%; unsaturation: 0.005 meq/g.

Polyol I: A 4000 mol. wt. (hydroxyl number = 28) propylene glycol-started, ethylene oxide-capped, propylene oxide-based polyether diol having a total oxyethylene content of about 20 wt.%; unsaturation: 0.005 meq/g.

Polyol J: A 4000 mol. wt. (hydroxyl number = 28) propylene glycol-started propylene oxide-based polyether diol; unsaturation: 0.015 meq/g.

Polyol K: A 6200 mol. wt. (hydroxyl number = 27) glycerin-started, ethylene oxide-capped, propylene oxide-based polyether triol having a total oxyethylene content of about 15 wt.%; unsaturation: 0.08 meq/g.

Polyol L: A 2000 mol. wt. (hydroxyl number = 56) propylene glycol-started, ethylene oxide-capped, propylene oxide-based polyether diol having a total oxyethylene content of about 45 wt.%; unsaturation: 0.02 meq/g.

Comparative Polyol 1 (CP-1): A 4000 mol. wt. (hydroxyl number = 28) propylene glycol-started, propylene oxide-based polyether diol; unsaturation: 0.08 meq/g.

Comparative Polyol 2 (CP-2): A 2000 mol. wt. (hydroxyl number = 56) polytetramethylene ether glycol. Commercially available from QO Chemicals as POLYMEG 2000.

Comparative Polyol 3 (CP-3): A 2000 mol. wt. (hydroxyl number = 56) polybutylene adipate diol. Commercially available from Bayer Corporation as DESMOPHEN 2502.

Comparative Polyol 4 (CP-4): A 1000 mol. wt. (hydroxyl number = 112) propylene glycol-started, propylene oxide-based polyether diol; unsaturation: 0.01 meq/g.

DETDA: An isomer mixture containing mostly 3,5-diethyl-2,4-toluenediamine and 3,5-diethyl-2,6-toluenediamine. Commercially available from Albemarle Corporation as ETHACURE 100.

DMTTDA: An isomer mixture containing mostly 3,5-dimethylthio-2,4-toluenediamine and 3,5-dimethylthio-2,6-toluenediamine. Commercially available from Albemarle Corporation as ETHACURE 300.

EXAMPLE 1

Preparation of Clear Polyurethane/Urea Elastomers

[0040]

Step 1: Polyol C (416 g) and 50% 4,4'-MDI (47.5 g) are charged to a one-liter, three-neck round-bottom flask equipped with thermocouple, stirrer, and nitrogen inlet. The mixture is stirred at 80°C for 5 h. Dibutyltin dilaurate (100 ppm) is added, and the reaction continues at 80°C for 30 min. The resulting isocyanate-terminated prepolymer has 1.40 wt.% NCO content (theoretical: 1.45 wt.%).

Step 2: Isophorone diisocyanate (IPDI) (37.0 g) is added to the prepolymer prepared in Step 1, and the mixture is heated and degassed under vacuum (80°C, < 1 mm Hg) for 20 min.

Step 3: The degassed prepolymer/IPDI mixture (171 g) at 80°C is poured into an 8-oz. jar and is then chain extended with DETDA (14.0 g) at room temperature using an NCO/NH ratio of 1.06. The mixture is stirred thoroughly for about 15 s, and is quickly cast into an open, preheated (100°C) block mold. The elastomer is cured at

100°C in a vented oven. The elastomers (4"x4"x1") are demolded within 5 min. and have excellent green strength. The elastomer samples are clear and have a rebound of 59%.

COMPARATIVE EXAMPLE 1

[0041]

Step 1: Polyol C (416 g), 50% 4,4'-MDI (47.5 g), and isophorone diisocyanate (37.0 g) are charged to a one-liter, three-neck round-bottom flask equipped as in Example 1. The mixture is heated with stirring at 80°C for 5 h. Dibutyltin dilaurate (100 ppm) is added, and heating continues at 80°C for 30 min. The resulting completely reacted isocyanate-terminated prepolymer has 3.97 wt.% NCO (theoretical value: 4.18 wt. % NCO).

Step 2: The prepolymer is heated and degassed under vacuum (80°C, < 1 mm Hg) for 20 min. The degassed prepolymer (171 g) at 80°C is poured into an 8-oz. jar and is then chain extended with DETDA (13.8 g) at room temperature using an NCO/NH ratio of 1.05. The mixture is stirred thoroughly for about 15 s, and is quickly cast into an open, preheated (100°C) block mold. The elastomer is cured at 100°C in a vented oven. The elastomers (4"x4"x1") are demolded within 5 min. and have excellent green strength. The elastomer samples are hazy.

EXAMPLES 2-3

[0042] The procedure of Example 1 is followed, except that Polyols G and I are used instead of Polyol C. The resulting elastomers are clear and have good rebound properties (see Table 1).

EXAMPLES 3-6 and COMPARATIVE EXAMPLE 2

Preparation of Clear Polyurethane/Urea Elastomers

[0043] The procedure of Example 1 is generally followed, but the amount of 50% 4,4'-MDI is varied to measure the effect of changing the prepolymer NCO/OH ratio. The amount of IPDI used is also varied to maintain a constant theoretical % NCO of 4.18% in the prepolymer/IPDI mixture. As Table 2 shows, elastomers made from prepolymers having NCO/OH = 1.8 to 2.6 are clear.

[0044] For Comparative Example 2, the procedure of Examples 3-6 is followed, except that enough 50% 4,4'-MDI is used to give a prepolymer NCO/OH ratio = 2.8. The elastomer made from this prepolymer is hazy (see Table 2).

EXAMPLES 7-8 and COMPARATIVE EXAMPLE 3

[0045] The procedure of Example 1 is generally followed, except that the overall % of 4,4'-MDI isomer used to make the prepolymer is varied from 50-80% to measure the effect of prepolymer 4,4'-MDI content on potlife. As Table 3 shows, clear elastomers with good resilience are obtained, and potlife is adequate (at least 20 seconds) within the range of 50-80% 4,4'-MDI content.

[0046] For Comparative Example 3, the procedure of Examples 7-8 is followed, except that the overall 4,4'-MDI isomer content used to make the prepolymer is 90%. While a clear elastomer having good resilience results, the potlife of this elastomer (about 15 seconds) is too short to allow casting of parts.

EXAMPLES 9-10 and COMPARATIVE EXAMPLE 4

[0047] These examples show the impact of polyol unsaturation on elastomer properties. The procedure of Example 1 is generally followed, except that the polyols used have varying degrees of unsaturation. As Table 4 shows, even a polyol with relatively high unsaturation (0.080 meq/g) gives a clear elastomer when the process of the invention is used. However, important properties such as resilience, hardness, tear strength, and especially tensile strength improve significantly when the polyol has lower unsaturation. As Example 9 and Comparative Example 4 demonstrate, tensile strength triples when the polyol unsaturation level drops from 0.08 to 0.005 meq/g.

EXAMPLES 11-14 and COMPARATIVE EXAMPLE 5

[0048] These examples show that the process of the invention gives clear elastomers with good resilience when TDI-80 is used to make the prepolymer. The procedure of Example 1 is generally followed, except that TDI-80 is used instead of 50% 4,4'-MDI. Table 5 summarizes the results. In Comparative Example 5, TDI-80 is used with Polyol B in the two-step process of Comparative Example 1. The resulting elastomer is hazy (see Table 5).

EXAMPLE 15 and COMPARATIVE EXAMPLES 6-7

[0049] A prepolymer is prepared from Polyol A (Mw/Mn=1.03) and TDI-80 according to the method of Example 11. The prepolymer is combined with IPDI in the usual way. The prepolymer/IPDI mixture has a viscosity of 720 cps at 80°C. Similar prepolymers are made using Comparative Polyol 2 (CP-2) (Mw/Mn=2.54) or Comparative Polyol 3 (CP-3) (Mw/Mn=2.45). The prepolymer/IPDI mixture from CP-2 has a viscosity of 5330 cps at 80°C. The prepolymer/IPDI mixture from CP-3 has a viscosity of 5350 cps at 80°C. Elastomers are formulated as in Example 11. The results, which Table 6 summarizes, indicate that prepolymer/aliphatic diisocyanate mixtures made from polyols having a Mw/Mn greater than about 1.5 are too viscous to process effectively in the process of the invention.

EXAMPLES 16-18

[0050] The procedure of Example 1 is generally followed, except that TDI-100 is used to make the prepolymer. As Table 7 shows, the resulting elastomers are clear, and they have exceptional resilience.

EXAMPLES 19-23 and COMPARATIVE EXAMPLE 8

[0051] The procedure of Example 1 is generally followed, except that TDI-100 is used to make the prepolymer. In addition, the amount of IPDI used is varied to measure the impact of higher % NCO content of the prepolymer/IPDI mixture on elastomer properties. As Table 8 shows, clear elastomers having good rebound properties result when the mixture % NCO content is less than about 14 wt.%. As Comparative Example 8 shows, a brittle product having poor green strength results when the mixture % NCO is 14 wt.%.

EXAMPLES 24-26

[0052] These examples show that the process of the invention applies generally to a variety of aliphatic diisocyanates. The procedure of Example 16 is generally followed with Polyol I, except that the aliphatic diisocyanate is varied from IPDI to H₁₂MDI or m-TMXDI. As Table 9 shows, clear elastomers with good hardness and resilience result. The less-reactive aliphatic diisocyanates (H₁₂MDI and m-TMXDI) give a generous potlife (100-150 seconds), which is excellent for hand casting.

EXAMPLE 27

[0053] The procedure of Example 1 is generally followed to make a clear polyurethane/urea elastomer using DMT-TDA as the chain extender as follows. The prepolymer is prepared from Polyol I (129.3 g) and TDI-100 (11.2 g). The NCO/OH ratio is 2.0. The prepolymer (140.5 g) is then combined with IPDI (9.4 g) to give a prepolymer/IPDI mixture having a theoretical wt.% NCO content of 4.18. The mixture (168 g) is chain extended with DMTTDA (ETHACURE 300, product of Albemarle Corp., 17.1 g) at 80°C. The potlife is about 300 seconds. After the usual curing at 100°C, elastomer samples are removed from the oven, allowed to cool for 60 min., and are demolded. Shore hardness: 72A; rebound: 66%; appearance: clear.

EXAMPLE 28

[0054] The procedure of Example 1 is generally followed to make a clear, relatively "soft" polyurethane/urea elastomer (Shore hardness = 67A) as follows. The prepolymer is prepared from Polyol I (1339 g) and TDI-100 (116 g). The NCO/OH ratio is 2.0. The prepolymer (1455 g) is then combined with IPDI (45 g) to give a prepolymer/IPDI mixture having a theoretical wt.% NCO content of 3.0 (actual: 2.9 wt.%). The mixture (174.4 g) is chain extended with DETDA (10.6 g) at 80°C. The potlife is about 105 seconds. After the usual curing at 100°C, elastomer samples are removed from the oven, allowed to cool for 10 min., and are demolded. Shore hardness: 67A; rebound: 78%; appearance: clear.

EXAMPLE 29

[0055] The procedure of Example 1 is generally followed to make a clear polyurethane/urea elastomer from a 6000 mol. wt. ethylene oxide-capped polyoxypropylene triol as follows. The prepolymer is prepared from Polyol K (427 g) and TDI-80 (31.6 g). The NCO/OH ratio is 1.8. The prepolymer (458 g) is then combined with IPDI (41.6 g) to give a prepolymer/IPDI mixture having a theoretical wt.% NCO content of 4.5 (actual: 4.3 wt.%). The mixture (170 g) is chain extended with DETDA (14.8 g) at 80°C. The potlife is about 40 seconds. After the usual curing at 100°C, elastomer samples are removed from the oven and demolded after 5 min. Shore hardness: 77A; rebound: 62%; appearance: clear.

COMPARATIVE EXAMPLE 9

[0056] This example (which is an example of the invention used for comparative purposes) shows that using a low molecular weight polyol can adversely impact elastomer resilience. The procedure of Example 1 is generally followed. The prepolymer is prepared from Polyol CP-4 (387 g) and TDI-80 (101 g). The NCO/OH ratio is 1.5. The prepolymer (488 g) is then combined with IPDI (12.3 g) to give a prepolymer/IPDI mixture having a theoretical wt.% NCO content of 4.18 (actual: 3.82 wt.%). The mixture (172 g) is chain extended with DETDA (13.2 g) at 80°C. The potlife is about 60 seconds. After the usual curing at 100°C, elastomer samples are removed from the oven and demolded after 10 min. Shore hardness: 80A; rebound: 44%; appearance: clear.

COMPARATIVE EXAMPLE 10

[0057] This example shows the effect of NCO/OH ratio on mixture viscosity. The procedure of Example 11 is followed, except that the NCO/OH ratio used is 1.20. The viscosity of the prepolymer/IPDI mixture is 10,300 cps (too viscous to process effectively). In contrast, the viscosity of the prepolymer/IPDI mixture prepared in Example 11 (NCO/OH ratio = 1:50) is 800 cps. The results show that a higher NCO/OH ratio greatly enhances elastomer processability.

EXAMPLES 30-31 and COMPARATIVE EXAMPLE 11

[0058] These examples show the effect of NCO/OH ratio on elastomer clarity using a 2000 mol. wt. EO-capped polyether diol. The procedure of Example 1 is generally followed. The prepolymer is prepared from Polyol L and 50% 4,4'-MDI (see Table 10 for amounts). The NCO/OH ratios range from 2.6 to 3.4. The prepolymer is combined with enough IPDI to give a prepolymer/IPDI mixture having a theoretical wt.% NCO content of 8.0. The mixture (160 g) is chain extended with DETDA (25.5 g) at 30°C. The potlife is about 20 seconds. After the usual curing at 100°C, elastomer samples are removed from the oven and demolded after 3 min. The samples made using an NCO/OH ratio of 2.6-3.0 are clear, while the one made at NCO/OH = 3.4 is hazy. The examples show that the NCO/OH ratio used in the process of the invention is important for getting clear elastomers.

[0059] The preceding examples merely illustrate the invention; the following claims define the scope of the invention.

Table 1:

Formulating Clear Elastomers with High Resilience	
Examples 1-3	
Step 1. NCO-terminated Prepolymer from 50% 4,4'-MDI	
50% 4,4'-MDI (g)	47
Polyol (g)	416
NCO/OH	1.8
Step 2. Mixture of Prepolymer and IPDI (Mixture Z)	
Prepolymer (g)	463
IPDI (g)	37
% NCO (theoretical)	4.18
Step 3. Elastomer Formulation	
Mixture Z (g)	171
DETDa (g)	14
Processing temp. (°C)	60-80
Potlife (s)	30-35
Demold time (min)	5

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Comparative Example 1: Prepolymer (from 50% 4,4'-MDI, Polyol C, and IPDI) chain extended with DETDA.				
		Elastomer Properties		
Ex #	Polyol	Shore hardness	Rebound (%)	Appearance
1	C	81A	59	clear
C1	C	78A	63	hazy
2	G	78A	61	clear
3	I	78A	61	dear

Table 2:

Effect of NCO/OH Ratio of Prepolymer on Elastomer Clarity	
Examples 3-6	
Step 1. NCO-terminated Prepolymer from 50% 4,4'-MDI and Polyol I	
50% 4,4'-MDI (g)	45-70 (see below)
Polyol I (g)	416
NCO/OH	1.8-2.8 (see below)
Step 2. Mixture of Prepolymer and IPDI (Mixture Z)	
Prepolymer (g)	463-485 (see below)
IPDI (g)	15-37 (see below)
% NCO (theoretical)	4.18
Step 3. Elastomer Formulation	
Mixture Z (g)	171
DETDA (g)	14
Processing temp. (°C)	60
Potlife (s)	20-30
Demold time (min)	5

Comparative Example 2: Same as above except that the NCO-terminated Prepolymer has NCO/OH = 2.8.					
	Prepolymer		Mixture		Elastomer
Ex #	4,4'-MDI (g)	NCO/OH	Prepolymer (g)	IPDI (g)	Appearance
3	45.4	1.8	463	37.4	clear
4	55.5	2.2	472	28.4	clear
5	60.5	2.4	476	23.9	clear
6	65.5	2.6	481	19.4	clear
C2	70.4	2.8	485	15.1	hazy

Table 3:

Effect of 4,4'-MDI Content on Potlife		
Examples 3, 7, and 8:		
Step 1.	NCO-terminated Prepolymer from Polyol I and 50% 4,4'-MDI or mixtures of 50% 4,4'-MDI and 100% 4,4'-MDI	
	Polyol I (g)	416
	50% 4,4'-MDI (g)	18-45 (see below)
	100% 4,4'-MDI (g)	0-27 (see below)
	NCO/OH	1.7-1.8
Step 2.	Mixture of Prepolymer and IPDI (Mixture Z)	
	Prepolymer (g)	462
	IPDI (g)	38
	% NCO (theoretical)	4.18
Step 3.	Elastomer Formulation	
	Mixture Z (g)	171
	DETDA (g)	14
	Processing temp. (°C)	60-80 (see below)
	Potlife (s)	20-30 (see below)
	Demold time (min)	5

Comparative Example 3: Same as above except that the ratio of 100% 4,4'-MDI to 50% 4,4'-MDI is increased to give 90% of 4,4'-MDI content overall.

Ex #	Prepolymer			Processing		Elastomer		
	50% 4,4'-MDI	100% 4,4'-MDI	overall % 4,4'-MDI	Temp (°C)	Pottlife (s)	Shore Hardness	Rebound	Appear.
3	45.4	0	50	60	30	78A	61	clear
7	26.1	18.2	70	80	25	77A	62	clear
8	17.7	26.6	80	80	20	76A	61	clear
C3	8.9	35.4	90	80	15*	76A	63	clear

* The pottlife of this sample is too short to allow casting of parts.

Table 4:

Effect of Polyol Unsaturation on Elastomer Properties		
Examples 9 and 10:		
Step 1.	NCO-terminated Prepolymer from 50% 4,4'-MDI	
	Polyol (g)	830 (see below)
	50% 4,4'-MDI (g)	105
	NCO/OH	1.9-2.0
Step 2.	Mixture of Prepolymer and IPDI (Mixture Z)	
	Prepolymer (g)	935
	IPDI (g)	65
	% NCO (theoretical)	4.18
Step 3.	Elastomer Formulation	
	Mixture Z (g)	171
	DETDA (g)	14
	Processing temp. (°C)	80
	Potlife (s)	30
	Demold time (min)	5

Comparative Example 4: Same as above except that the Polyol used (CP-1) has a much higher degree of unsaturation (0.08 meq/g).

Ex #	Prepolymer		Elastomer					
	Polyol	Unsat. (meq/g)	Tensile str. (psi)	Tear str. (pli)	Elong. (%)	Shore Hardness	Rebound (%)	Appear.
9	C	0.005	3760	380	950	80A	59	clear
10	J	0.015	2930	380	1230	78A	58	clear
C4	CP-1	0.080	1270	280	1200	76A	55	clear

C4 is an example of the invention used for comparative purposes.

Table 5:

Formulating Clear Elastomers with High Resilience: TDI-80 Systems		
Examples 11-14		
Step 1.	NCO-terminated Prepolymer from Polyol and TDI-80	
	Polyol (g)	414-425 (see below)
	TDI-80 (g)	35-54 (see below)
	NCO/OH	1.50
Step 2.	Mixture of Prepolymer and IPDI (Mixture Z)	
	Prepolymer (g)	460-468 (see below)
	IPDI (g)	32-40 (see below)
	% NCO (theoretical)	4.18
Step 3.	Elastomer Formulation	
	Mixture Z (g)	171
	DETDA (g)	14
	Processing temp. (°C)	80

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Table 5: (continued)

Formulating Clear Elastomers with High Resilience: TDI-80 Systems		
Examples 11-14		
Step 3.	Elastomer Formulation	
	Pottlife (s)	55-65
	Demold time (min)	8-9

Comparative Example 5: Prepolymer (from TDI-80, Polyol B, and IPDI) chain extended with DETDA.

	Prepolymer			Mixture		Elastomer		
Ex #	Polyol	Amt. (g)	TDI-80 (g)	Prepolymer (g)	IPDI (g)	Shore Hardness	Rebound (%)	Appear.
11	B	414	54.1	468	32.2	79A	60	clear
C5	B	413	54.3	467	32.2	80A	66	hazy
12	H	417	48.7	466	34.5	78A	64	clear
13	E	424	36.9	461	39.6	76A	62	clear
14	F	425	34.6	459	40.5	76A	63	clear

Table 6:

Effect of Polyol Molecular Weight Distribution on Viscosity of the Prepolymer/Aliphatic Diisocyanate Mixture							
Example 15 and Comparative Examples 6-7:							
Step 1.	NCO-terminated Prepolymer from Polyol and TDI-80						
	<table> <tr> <td>Polyol (see below) (g)</td><td>414</td></tr> <tr> <td>TDI-80 (g)</td><td>54.1</td></tr> <tr> <td>NCO/OH</td><td>1.50</td></tr> </table>	Polyol (see below) (g)	414	TDI-80 (g)	54.1	NCO/OH	1.50
Polyol (see below) (g)	414						
TDI-80 (g)	54.1						
NCO/OH	1.50						
Step 2.	Mixture of Prepolymer and IPDI (Mixture Z)						
	<table> <tr> <td>Prepolymer (g)</td><td>468</td></tr> <tr> <td>IPDI (g)</td><td>32.2</td></tr> <tr> <td>% NCO (theoretical)</td><td>4.18</td></tr> </table>	Prepolymer (g)	468	IPDI (g)	32.2	% NCO (theoretical)	4.18
Prepolymer (g)	468						
IPDI (g)	32.2						
% NCO (theoretical)	4.18						

Ex #	Polyol	Mw/Mn	Prepolymer/IPDI Mixture Viscosity (cps, at 80°C)
15	A	1.03	720
C6	CP-2	2.54	5330
C7	CP-3	2.45	5350

Table 7:

Formulating Clear Elastomers with High Resilience: TDI-100 Systems		
Examples 16-18		
Step 1.	NCO-terminated Prepolymer from Polyol and TDI-100	
	Polyol (g)	414-428 (see below)
	TDI-100 (g)	46-72 (see below)
	NCO/OH	2.00
Step 2.	Mixture of Prepolymer and IPDI (Mixture Z)	
	Prepolymer (g)	472-486 (see below)
	IPDI (g)	14-28 (see below)
	% NCO (theoretical)	4.18-4.50 (see below)
Step 3.	Elastomer Formulation	
	Mixture Z (g)	171
	DETDA (g)	14
	Processing temp. (°C)	80
	Potlife (s)	65-80
	Demold time (min)	10

Ex #	Prepolymer			Mixture		Elastomer		
	Polyol	Amt. (g)	TDI-100 (g)	Prepolymer (g)	IPDI (g)	Shore Hardness	Rebound (%)	Appear.
16	B	414	72.0	486	13.7	80A	67	clear
17	D	423	49.2	472	28.1	80A	68	clear
18	F	428	46.4	474	25.7	76A	71	clear
Prepolymer Exs. 16-17: %NCO = 4.50; Ex. 18: % NCO = 4.18								

Table 8:

Effect of Mixture % NCO Content on Elastomer Properties: TDI-100 Systems		
Examples 19-23		
Step 1. NCO-terminated Prepolymer from Polyol H and TDI-100		
Polyol H (g)		129-168 (see below)
TDI-100 (g)		19-25 (see below)
NCO/OH		1.90
Step 2. Mixture of Prepolymer and IPDI (Mixture Z)		
Prepolymer (g)		148-193 (see below)
IPDI (g)		7.2-52 (see below)
% NCO (theoretical)		4.2-12 (see below)
Step 3. Elastomer Formulation		
Mixture Z (g)		171-149 (see below)
DETDA (g)		14-36 (see below)
Processing temp. (°C)		50-80
Potlife (s)		20-70
Demold time (min)		5-10

Comparative Example 8: Prepared as in Examples 19-23, except that the ratio of IPDI to Prepolymer is higher, giving a Mixture with 14 wt.% NCO content.

Ex #	Prepolymer		Mixture			Elastomer				
	Polyol H (g)	TDI-100 (g)	Prepol. (g)	IPDI (g)	% NCO	Mixture Z (g)	DETDA (g)	Hard.	Reb'd (%)	Appear.
19	168	24.7	193	7.2	4.18	171	14.4	79A	72	clear
20	159	23.4	182	17.6	6.00	165	20.0	90A	62	clear
21	149	22.0	171	29.0	8.00	159	25.7	42D	59	clear
22	139	20.5	160	40.5	10.0	154	31.1	53D	59	clear
23	129	19.0	148	52.1	12.0	149	36.1	61D	59	clear
C8	119	17.5	137	63.5	14.0	144	40.8	*	*	clear

* Brittle product, poor green strength; not tested.

Table 9:

Clear Elastomers: TDI-100 Systems: Effect of Aliphatic Diisocyanate	
Examples 24-26	
Step 1. NCO-terminated Prepolymer from Polyol I and TDI-100	
Polyol 1 (g)	128
TDI-100 (g)	11.1
NCO/OH	2.0
Step 2. Mixture of Prepolymer and IPDI (Mixture Z)	
Prepolymer (g)	140
Aliphatic diisocyanate (g)	9-11 (see below)
% NCO (theoretical)	4.18
Step 3. Elastomer Formulation	
Mixture Z (g)	171
DETDA (g)	14.4
Processing temp. (°C)	80
Potlife (s)	70-150 (see below)
Demold time (min)	9-45 (see below)

Ex #	Mixture		Processing		Elastomer		
	Aliphatic Diisocyanate	Amt. (g)	Potlife (s)	Demold (min)	Shore Hardness	Rebound (%)	Appearance
24	IPDI	9.4	70	9	77A	68	clear
25	H ₁₂ MDI	11.3	100	10	82A	67	clear
26	m-TMXDI	10.4	150	45	76A	65	clear

Table 10:

Effect of NCO/OH Ratio on Elastomer Clarity	
Examples 30-31 and Comparative Example 12:	
Step 1. NCO-terminated Prepolymer from Polyol L and 50% 4,4'-MDI	
Polyol L (g)	340-344 (see below)
50% 4,4'-MDI (g)	112-145 (see below)
NCO/OH	2.6-3.4 (see below)
Step 2. Mixture of Prepolymer and IPDI (Mixture Z)	
Prepolymer (g)	455-485 (see below)
IPDI (g)	15-45 (see below)
% NCO (theoretical)	8.0
Step 3. Elastomer Formulation	
Mixture Z (g)	160
DETDA (g)	25.5
Processing temp. (°C)	30
Potlife (s)	20
Demold time (min)	3

	Prepolymer			Mixture		Elastomer
Ex #	Polyol L (g)	50% 4,4'-MDI (g)	NCO/OH	Prepolymer (g)	IPDI (g)	Appearance
30	344	112	2.6	455	44.7	clear
31	342	128	3.0	470	29.9	clear
C12	340	145	3.4	485	15.1	hazy

Claims

1. A process for producing a clear polyurethane/urea elastomer where "clear" signifies that a person can easily read newsprint through the 10,16 cm (4") length of a 10,16 cm x 2,54 cm x 2,54 cm (4"x 1"x 1") sample and the sample appears clear even through the 10,16 cm (4") thickness, comprising

(a) reacting an aromatic diisocyanate comprising less than 90wt% of 4,4'-MDI with a polyol having a polydispersity (Mw/Mn) less than 1.5 to produce an isocyanate-terminated prepolymer, wherein the NCO/OH mole ratio is within the range of 1.3 to 3.0;

(b) mixing the prepolymer with an aliphatic diisocyanate to form a prepolymer/aliphatic diisocyanate mixture that has an NCO content within the range 2 to 13 wt.%; and

(c) reacting the prepolymer/aliphatic diisocyanate mixture with an aromatic diamine, wherein the aromatic diamine is used at an NCO/NH ratio in the range of 0.9 to 1.2.

2. The process of claim 1 wherein the aromatic diisocyanate is selected from the group consisting of toluene diisocyanates and MDIs that contain at least 15 wt.% of MDI isomers other than 4,4'-MDI.
3. The process of any preceding claim wherein the polyol has an Mw/Mn of less than 1.4.
4. The process of any preceding claim wherein the polyol has an Mw/Mn of less than 1.2.

5. The process of any preceding claim wherein the polyol has an unsaturation less than 0.02 meq/g.
6. The process of any preceding claim wherein the polyol has an unsaturation less than 0.01 meq/g.
7. The process of any preceding claim wherein the polyol has an equivalent weight within the range of 750 to 10,000.
8. The process of any preceding claim wherein the prepolymer is made at an NCO/OH ratio within the range of 1.5 to 2.0.
9. The process of any preceding claim wherein the prepolymer is made at an NCO/OH ratio within the range of 1.5 to 1.8.
10. The process of any preceding claim wherein the aliphatic diisocyanate is selected from the group consisting of hydrogenated MDIs, isophorone diisocyanate, tetramethylxylene diisocyanates (TMXDIs), and mixtures thereof.
11. The process of any preceding claim wherein the NCO content of the prepolymer/aliphatic diisocyanate mixture is within the range of 3 to 10 wt.%.
12. The process of any preceding claim wherein the aromatic diamine is selected from the group consisting of diethyltoluenediamines (DETDA), dimethylthiitoluene diamines (DMTTDA), and mixtures thereof.
13. The process of any preceding claim wherein the aromatic diamine has a Gardner color less than or equal to 7.
14. The process of any preceding claim wherein the aromatic diamine has a Gardner color less than or equal to 3.
15. The process of any preceding claim wherein the elastomer produced has a Shore hardness of at least 75A.
16. The process of any preceding claim wherein the elastomer produced has a resilience of at least 55%.
17. The process of any preceding claim wherein the elastomer produced has a resilience of at least 65%.
18. A polyurethane/urea elastomer made by the process of any preceding claim.
19. An in-line skate or skateboard wheel fabricated from the elastomer of claim 18.
20. A process which comprises:
 - (a) reacting an aromatic diisocyanate with a polyether diol having a polydispersity (M_w/M_n) less than 1.2 and an unsaturation less than 0.007 meq/g to produce an isocyanate-terminated prepolymer, wherein the NCO/OH mole ratio is within the range of 1.5 to 1.8;
 - (b) mixing the prepolymer with an aliphatic diisocyanate selected from the group consisting of hydrogenated MDIs, isophorone diisocyanate, tetramethylxylene diisocyanates (TMXDIs), and mixtures thereof to form a prepolymer/aliphatic diisocyanate mixture that has an NCO content within the range of 3 to 10wt.%; and
 - (c) reacting the prepolymer/aliphatic diisocyanate mixture with an aromatic diamine selected from the group consisting of diethyltoluenediamines (DMTTDA), and mixtures thereof, wherein the aromatic diamine or mixture thereof is used at an NCO/NH ratio in the range of 0.9 to 1.2.
21. A polyurethane/urea elastomer made by the process of claim 20.
22. An in-line skate or skateboard wheel fabricated from the elastomer of claim 21.

Patentansprüche

1. Verfahren zur Herstellung eines klaren Polyurethan/Harnstoff-Elastomers, wobei "klar" bedeutet, dass eine Person durch die Länge von 10,16 cm (4") einer Probe von 10,16 cm×2,54 cm×2,54 cm (4"×1"×1") leicht eine Zeitung

lesen kann, und die Probe durch die Dicke von 10,16 cm (4") klar erscheint, umfassend

- (a) die Umsetzung eines aromatischen Diisocyanats, das weniger als 90 Gew.-% 4,4'-MDI umfasst, mit einem Polyol einer Polydispersität (M_w/M_n) von weniger als 1,5, um ein isocyanat-terminiertes Prepolymer herzustellen, wobei das NCO/OH-Stoffmengenverhältnis im Bereich von 1,3 bis 3,0 liegt;

(b) das Vermischen des Prepolymers mit einem aliphatischen Diisocyanat, um ein Gemisch von Prepolymer/aliphatischem Diisocyanat zu bilden, das einen NCO-Gehalt im Bereich von 2 bis 13 Gew.-% aufweist, und

(c) die Umsetzung des Gemischs von Prepolymer/aliphatischem Diisocyanat mit einem aromatischen Diamin, wobei das aromatische Diamin in einem NCO/NH-Verhältnis im Bereich von 0,9 bis 1,2 verwendet wird.
2. Verfahren gemäß Anspruch 1, wobei das aromatische Diisocyanat aus der Gruppe ausgewählt ist, bestehend aus Toluoldiisocyanaten und MDIs, die wenigstens 15 Gew.-% MDI-Isomere enthalten, die von 4,4'-MDI verschieden sind.
3. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Polyol ein M_w/M_n von weniger als 1,4 aufweist.
4. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Polyol ein M_w/M_n von weniger als 1,2 aufweist.
5. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Polyol eine Nichtsättigung von weniger als 0,02 Milliäquivalenten/g aufweist.
6. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Polyol eine Nichtsättigung von weniger als 0,01 Milliäquivalenten/g aufweist.
7. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Polyol ein Äquivalentgewicht im Bereich von 750 bis 10 000 aufweist.
8. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Prepolymer bei einem NCO/OH-Verhältnis im Bereich von 1,5 bis 2,0 hergestellt wird.
9. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das Prepolymer bei einem NCO/OH-Verhältnis im Bereich von 1,5 bis 1,8 hergestellt wird.
10. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das aliphatische Diisocyanat aus der Gruppe ausgewählt ist, die aus hydrierten MDIs, Isophorondiisocyanat, Tetramethylxyloldiisocyanaten (TMXDIs) und deren Mischungen besteht.
11. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem der NCO-Gehalt des Gemisches von Prepolymer/aliphatischem Diisocyanat im Bereich von 3 bis 10 Gew.-% liegt.
12. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das aromatische Diamin aus der Gruppe ausgewählt ist, die aus Diethyltoluoldiaminen (DETDA), Dimethylthiotoluoldiaminen (DMTTDA) und deren Mischungen besteht.
13. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das aromatische Diamin eine Gardner-Farbzahl von weniger als 7 oder gleich 7 hat.
14. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das aromatische Diamin eine Gardner-Farbzahl von weniger als 3 oder gleich 3 hat.
15. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das hergestellte Elastomer eine Shore Härte von wenigstens 75A hat.
16. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das hergestellte Elastomer eine elastische Erholung von wenigstens 55 % hat.

17. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, in dem das hergestellte Elastomer eine elastische Erholung von wenigstens 65 % hat.

18. Polyurethan/Harnstoff-Elastomer, das durch das Verfahren gemäß irgendeinem der vorhergehenden Ansprüche hergestellt wird.

19. In-line-Skate-Rolle oder Skateboard-Rolle, die aus dem Elastomer gemäß Anspruch 18 hergestellt wird.

20. Verfahren, umfassend

(a) die Umsetzung eines aromatischen Diisocyanats mit einem Polyetherdiol, das eine Polydispersität (M_w/M_n) von weniger als 1,2 und eine Nichtsättigung von weniger als 0,007 Milliäquivalenten/g aufweist, um ein isocyanat-terminiertes Prepolymer herzustellen, wobei das NCO/OH-Stoffmengenverhältnis im Bereich von 1,5 bis 1,8 liegt;

(b) das Vermischen des Präpolymers mit einem aliphatischen Diisocyanat, das aus der Gruppe ausgewählt ist, die aus hydrierten MDIs, Isophorondiisocyanat, Tetramethylxyldiisocyanaten (TMXDIs) und deren Mischungen besteht, um ein Gemisch von Prepolymer/aliphatischem Diisocyanat herzustellen, das einen NCO-Gehalt im Bereich von 3 bis 10 Gew.-% aufweist; und

(c) die Umsetzung des Gemisches von Prepolymer/aliphatischem Diisocyanat mit einem aromatischen Diamin, das aus der Gruppe ausgewählt ist, die aus Diethyltoluoldiaminen (DETDA), Dimethylthiotoluoldiaminen (DMTTDA) und deren Mischungen besteht, wobei das aromatische Diamin oder deren Mischung bei einem NCO/OH-Verhältnis im Bereich von 0,9 bis 1,2 verwendet wird.

21. Polyurethan/Harnstoff Elastomer, das durch das Verfahren gemäß Anspruch 20 hergestellt wird.

22. In-line-Skate-Rolle oder Skateboard-Rolle, die aus dem Elastomer gemäß Anspruch 21 hergestellt wird.

Revendications

1. Procédé de préparation d'un élastomère clair de polyuréthane/urée, où « clair », signifie qu'une personne peut facilement lire un papier journal au travers de la longueur de 10,16 cm (4") d'un échantillon de 10,16 cm x 2,54 cm x 2,54 cm (4"x1"x1"), et l'échantillon semble clair même au travers de l'épaisseur de 10,16 cm (4"), comprenant :

(a) la réaction d'un diisocyanate aromatique comprenant moins de 90% en poids de 4,4'-MDI avec un polyol ayant une polydispersité (M_w/M_n) inférieure à environ 1,5 pour donner un prépolymère à terminaison isocyanate, où le rapport molaire NCO/OH se situe dans l'intervalle allant de 1,3 à 3,0 ;

(b) le mélange du prépolymère à un diisocyanate aliphatique pour former un mélange prépolymère/diisocyanate aliphatique, qui a une teneur en NCO située dans l'intervalle allant de 2 à 13% en poids, et

(c) la réaction du mélange prépolymère/diisocyanate aliphatique avec une diamine aromatique, où la diamine aromatique est utilisée en un rapport NCO/NH situé dans l'intervalle allant de 0,9 à 1,2.

2. Procédé selon la revendication 1, dans lequel le diisocyanate aromatique est choisi parmi le groupe consistant en les toluènediisocyanates et les MDI qui contiennent au moins 15% en poids d'isomères MDI autres que la 4,4'-MDI.

3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyol a un M_w/M_n inférieur à 1,4.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyol a un M_w/M_n inférieur à 1,2.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyol a une insaturation inférieure à 0,02 méq/g.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyol a une insaturation inférieure à 0,01 méq/g.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyol a un poids équivalent situé dans l'intervalle allant de 750 à 10 000.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le prépolymère est composé d'un rapport NCO/OH situé dans l'intervalle allant de 1,5 à 2,0.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le prépolymère est composé d'un rapport NCO/OH situé dans l'intervalle allant de 1,5 à 1,8.
10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le diisocyanate aliphatique est choisi parmi le groupe consistant en les MDI hydrogénés, l'isophoronediiisocyanate, les tétraméthylxylènediisocyanates (TMXDI) et leurs mélanges.
11. Procédé selon l'une quelconque des revendications précédentes, dans lequel la teneur en NCO du mélange prépolymère/diisocyanate aliphatique se situe dans l'intervalle allant de 3 à 10% en poids.
12. Procédé selon l'une quelconque des revendications précédentes, dans lequel la diamine aromatique est choisie parmi le groupe consistant en les diéthyltoluènediamines (DETDA), les diméthylthiotoluènediamines (DMTTDA) et leurs mélanges.
13. Procédé selon l'une quelconque des revendications précédentes, dans lequel la diamine aromatique a une couleur suivant Gardner inférieure à ou égale à 7.
14. Procédé selon l'une quelconque des revendications précédentes, dans lequel la diamine aromatique a une couleur suivant Gardner inférieure à ou égale à 3.
15. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'élastomère produit a une dureté Shore d'au moins 75A.
16. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'élastomère produit a une résilience d'au moins 55%.
17. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'élastomère produit a une résilience d'au moins 65%.
18. Elastomère de polyuréthane/urée préparé par le procédé selon l'une quelconque des revendications précédentes.
19. Roue de patin à roues alignées ou de planche à roulettes, préparée à partir de l'élastomère selon la revendication 18.
20. Procédé qui comprend :
 - (a) la réaction d'un diisocyanate aromatique avec un polyéther-diol ayant une polydispersité (M_w/M_n) inférieure à 1,2 et une insaturation inférieure à 0,007 méq/g pour donner un prépolymère à terminaison isocyanate, où le rapport molaire NCO/OH se situe dans l'intervalle allant de 1,5 à 1,8 ;
 - (b) le mélange du prépolymère avec un diisocyanate aliphatique choisi parmi le groupe consistant en les MDI hydrogénés, l'isophoronediiisocyanate, les tétraméthylxylènediisocyanates (TMXDI) et leurs mélanges, pour former un mélange prépolymère/diisocyanate aliphatique, qui a une teneur en NCO située dans l'intervalle allant de 3 à 10% en poids; et
 - (c) la réaction du mélange prépolymère/diisocyanate aliphatique avec une diamine aromatique choisie parmi le groupe consistant en les diéthyltoluènediamines (DETDA), les diméthylthiotoluènediamines (DMTTDA) et leurs mélanges, où la diamine aromatique ou le mélange est utilisé en un rapport NCO/NH situé dans l'intervalle allant de 0,9 à 1,2.
21. Elastomère de polyuréthane/urée préparée par le procédé de la revendication 20.
22. Roue de patin à roues alignées ou de planche à roulettes, préparée à partir de l'élastomère selon la revendication 21.

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